Translation of JP-A 62-60640

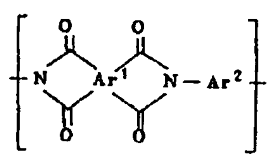
SPECIFICATION

1. Title of the Invention:

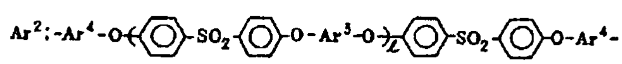
LAMINATE OF METAL AND RESIN

2. Claim:

1. A laminate comprising a thermoplastic polyimide of a general formula:



wherein Ar^2 represents


,

Ar^1 represents a residue of an aromatic tetracarboxylic acid,

Ar^3 represents a residue of a diphenol,

Ar^4 represents a residue of an aminophenol,

1 indicates a mean value of integers having a certain distribution between 0 and 50, and is a number of from 0.5 to 20,

and a metal.

3. Detailed Description of the Invention:

Industrial Field of Application

The present invention relates to a laminate comprising a specific thermoplastic polyimide resin and a metal, and to a method for producing it. More precisely, the invention relates to a laminate that comprises a specific thermoplastic polyimide resin and a metal directly bonded to each other, and to a method for producing it.

Prior Art

For the laminate of the type, those fabricated by laminating a thermosetting epoxy resin or phenolic resin and metal foil via an epoxy or modified phenolic adhesive layer therebetween have heretofore been put into wide practical use. Other laminates of further improved heat resistance, which comprise a resin layer of diallyl phthalate resin, polyimide resin or maleimide resin and metal foil bonded to each other via a third adhesive layer therebetween, have also been put into practical use. As still other laminates of thermoplastic resin and metal, some examples of laminates of polyether imide (ULTEM) and copper foil are reported in *Insulation Circuit*, October 1982.

Thermofusible polyether sulfonimide of good heat resistance is disclosed in JP-A 58-9426.

Problems to be solved by the Invention

Thermosetting resin (e.g., epoxy resin, phenolic resin) requires curing in order that it may sufficiently exhibit its

performance, and therefore production of laminates with the resin takes a lot of time. In addition, the dielectric constant of the resin layer is generally high, and the applicability of the resin to substrates for printed circuit boards is limited.

The adhesiveness of conventional polyimide resin, diallyl phthalate resin and fluororesin to metal is not good. Therefore, when laminates of the resin and metal are fabricated, generally employed is a method of putting an adhesive layer between the two. In this case, however, the heat resistance of the adhesive is not always satisfactory and the power of the adhesive may often lower at high temperatures. To that effect, therefore, the heat-resistant temperature of the laminates shall be determined by the heat-resistant temperature of the adhesive, and this means that the heat resistance intrinsic to the resin is not sufficiently utilized in most laminates of the type. Laminates of a certain type of thermoplastic resin and metal are known, but their application is limited in point of the heat-resistant temperature thereof since the heat resistance of the resin itself is not always satisfactory.

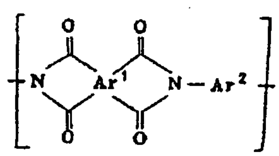
Means for Solving the Problems

We, the present inventors have assiduously studied so as to obtain a laminate of resin and metal which is satisfactorily resistant to heat and which can be readily fabricated and, as a result, have found that a laminate that comprises a specific thermoplastic polyimide and metal has high adhesion strength

even though no adhesive is used therein and, in addition, its heat resistance is good and it is resistant to flames and has good electric characteristics, or that is, the laminate has good properties. On the basis of these findings, we have reached the present invention.

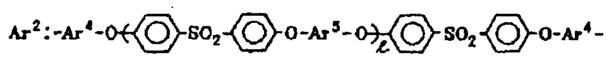
Specifically, the invention relates to a laminate that comprises a specific thermoplastic polyimide resin and a metal directly bonded to each other with no adhesive of a different type therebetween, and to a method for producing it.

The thermoplastic polyimide resin for use in the invention is represented by a general formula (I):



(I)

wherein Ar^2 represents



(II),

Ar^1 represents a residue of an aromatic tetracarboxylic acid,

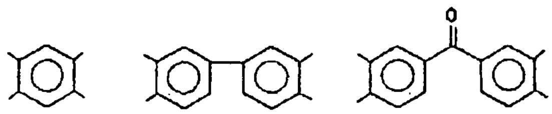
Ar^3 represents a residue of a diphenol,

Ar^4 represents a residue of an aminophenol,

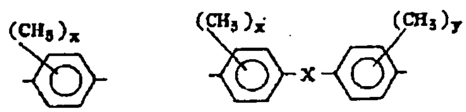
l indicates a mean value of integers having a certain distribution between 0 and 50, and is a number of from 0.5 to 20.

In formula (I), Ar^1 is a residue of an aromatic

tetracarboxylic acid, preferably the following:

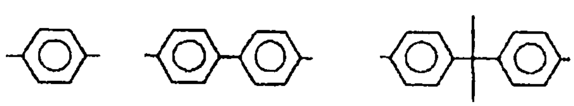


Ar^2 is a residue of a diamine of formula (II). In formula (II), Ar^3 is a residue of a diphenol, preferably the following:

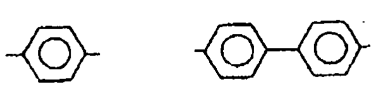


In these, X represents a direct bond, -O-, -S-, $-SO_2-$, -CO-, an alkylene or alkylidene group having from 1 to 6 carbon atoms; and x and y independently indicate 0, 1 or 2.

Copolymers with no aliphatic group in Ar^3 generally have a high glass transition temperature and their thermal aging resistance is good. Ar^3 is preferably the following:



In view of the durability of the resin, Ar^3 is more preferably the following:



In formula (II), Ar^4 is a residue of an aminophenol, preferably the following:

For it, paraphenylene is preferred to metaphenylene, since it may increase the glass transition temperature of the copolymers with it.

In formula (II), l indicates a mean value of integers having a certain distribution between 0 and 50, and is a number of from 0.5 to 20, preferably $1 < l < 9$.

Stabilizer such as polycarboxylate or colorant, and even glass fibers and other inorganic substances may be added with no problem to the specific thermoplastic polyimide resin for use in the invention.

The metal for use in the invention is selected from those usable for electric connection, preferably gold, silver, copper, nickel, aluminium. More preferably, it is copper.

The thickness of the metal to be in the tabular laminates of the invention may be from 0.0001 μm to 5 mm, preferably from 1 μm to 5 mm, more preferably from 5 μm to 5 mm. The diameter of the metal to be in the cable laminates of the invention may be from 0.0001 to 300 mm, preferably from 0.01 to 100 mm.

Regarding the method of producing the laminates of the invention, for example, the temperature may fall between 260

and 420°C, preferably between 300 and 390°C, and the pressure may fall between 1 and 1000 kg/cm^2 in compression molding to produce them. The laminates may also be produced continuously in a mode of extrusion forming. Not laminated with metal, the resin may be plated with metal through chemical plating, electroplating, sputtering or vapor deposition to produce the laminates of the invention.

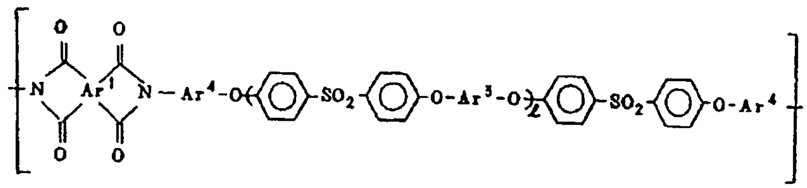
Advantages of the Invention

The laminate of the invention may be produced in a more simplified manner than any other conventional laminates since it does not use adhesive, and, in addition, its adhesiveness is good. Further, the heat resistance and the flame retardancy of the laminate are both good, and the laminate can be used even at high temperatures. Accordingly, the laminate is suitable to electronic materials which are exposed to high temperatures as comprising devices that generate much heat.

The invention is described concretely with reference to the following Examples, to which, however, the invention is not limited.

Examples

In the following Examples, specific thermoplastic polyimides of the following formula are used.



(III)

Comparative Example:

Copper foil of 35 μm thick was bonded to Union Carbide's polyether sulfone (PES) of the following formula. A press was used for bonding the copper foil thereto, at a predetermined temperature and under a predetermined pressure as in Table 1. The resulting laminate was patterned and its peeling strength was measured, according to JIS-C-6481. The result is given in Table 1.

Examples 1 to 5:

Copper foil of 35 μm thick was bonded to a thermoplastic polyimide of formula (III). The logarithmic viscosity of the resin falls between 0.45 and 0.49, measured in N-methyl-2-pyrrolidone to have a concentration of 0.5 g/dl at 30°C. A press was used for bonding the copper foil thereto, at a predetermined temperature and under a predetermined pressure as in Table 1. The resulting laminate was patterned and its peeling strength was measured, according to JIS-C-6481. The result is given in Table 1. From Table 1, it is understood that the laminates of the invention well satisfy the peeling strength 1.4 kg/cm necessary for substrates for printed circuit boards.

Examples 6 to 8:

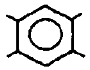
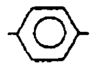
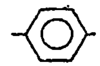
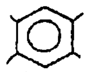
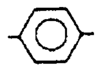
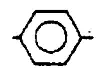
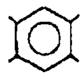
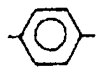
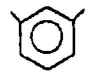
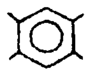
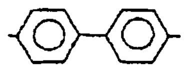
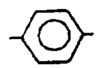
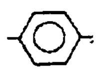
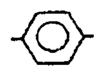
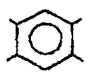
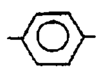
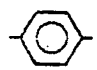
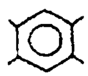
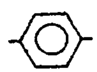
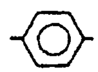
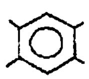
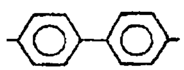
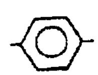
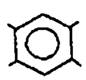
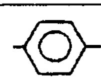
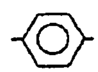
Using an extruder, 20 parts by weight of glass short fibers were kneaded with a thermoplastic polyimide of formula (III)

at 360°C. The logarithmic viscosity of the resin falls between 0.42 and 0.44, measured in N-methyl-2-pyrrolidone to have a concentration of 0.5 g/dl at 30°C. The resulting mixture was processed and measured in the same manner as in Examples 1 to 5. The result is given in Table 1. From Table 1, it is understood that the laminates of the invention well satisfy the peeling strength 1.4 kg/cm necessary for substrates for printed circuit boards.

Example 9:

Using an extruder, 20 parts by weight of glass short fibers were kneaded with a thermoplastic polyimide of formula (III) at 360°C. The logarithmic viscosity of the resin is 0.44, measured in N-methyl-2-pyrrolidone to have a concentration of 0.5 g/dl at 30°C. Using an injection molding machine, the resulting mixture was cast into a sheet of 100 × 100 mm. The nozzle temperature was 360°C; the front temperature was 370°C; and the back side temperature was 350°C. Copper was deposited on the sheet in a mode of chemical plating. The peeling strength of the plated sheet was measured according to JIS-C-6481, and the result is given in Table 1. When an ordinary polymer material is chemically plated with no surface treatment thereof, then the plating layer expands and peels. However, the laminate of the invention had a smooth surface.

Table 1

Example	Ar^1	Ar^3	Ar^4	l	Press Temperature °C	Press Pressure kg/cm	Peeling Strength kg/cm	Soldering Heat Resistance °C/sec
1				3.05	320	150	1.8	260/120<
2				3.05	380	100	2.2	260/120<
3				2.5	340	150	2.0	260/100<
4				4.1	360	100	2.0	290/120<
5				2.9	310	100	1.7	260/100<
6				3.05	340	200	1.5	280/120<
7				3.05	380	100	1.7	280/120<
8				4.05	380	100	1.8	290/120<
9				3.05	-	-	0.5	-
Comparative Example	-	-	-	-	330	200	0.9	260/10<